



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| <b>(51) International Patent Classification <sup>6</sup> :</b><br><b>A01N 33/08, 33/12, 33/24, 59/00, 59/06, 59/16</b>  | <b>A1</b> | <b>(11) International Publication Number:</b> <b>WO 97/24926</b><br><b>(43) International Publication Date:</b> 17 July 1997 (17.07.97)   |
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| <b>(54) Title:</b> REST-BREAKING COMPOSITIONS COMPRISING ACTIVITY PROMOTING ADDITIVES<br><br><b>(57) Abstract</b><br><br>Rest-breaking compositions are disclosed comprising at least one rest-breaking agent selected from the group of calcium nitrate, ammonium nitrate, calcium ammonium nitrate, urea ammonium nitrate, and zinc ammonium nitrate, in conjunction with one or more activity promoting additives selected from the the group of alkoxyated amines, quaternary ammonium compounds and amine oxides. Further a process for breaking the rest of deciduous fruit trees is disclosed. The activity promoting additives enhance the activity of rest-breaking agents thereby leading to improvements in the yields and quality of fruit from deciduous fruit trees in regions which have mild winter weather conditions. |           |   |

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## Rest-Breaking Compositions Comprising Activity Promoting Additives

The present invention relates to new rest-breaking compositions comprising at least one rest-breaking agent and one or more activity  
5 promoting additives, and to the use of these compositions for enhancing the rest-breaking in deciduous fruit trees.

### Background of the invention

10 Deciduous fruit trees require winter chilling to grow normally. The amount of chilling required depends upon the kind of fruit and the cultivar. If winter chilling is insufficient, then growth abnormalities such as delayed and uneven blossoming, poor leaf cover, insufficient fruit-set and reduced fruit  
15 size can occur. These symptoms are generally referred to as delayed foliation according to the article, Blommaert, K.L.J., "Winter Dormancy and Delayed Foliation," The Deciduous Fruit Grower, (1956).

Measures to reduce the symptoms of delayed foliation include treatment with high volumes of chemical rest-breaking agents during later winter and  
20 various physical manipulations such as pruning.

In South Africa, for example, most apple trees receive insufficient winter chilling to break rest completely and thus annual application of a chemical rest-breaking agent is standard practice. The most widely used rest-  
25 breaking agent in commercial apple orchards is dinitro-ortho-cresol (DNOC) in combination with winter-oil emulsion (a lipophilic agent) (Erez, A. et al., "Improved Methods of Breaking Rest in the Peach and Other Deciduous Fruit Species," J. Amer. Soc. Hort. Sci., 96, pp. 519-522 (1971)). This

article also mentions the use of the potassium salt of gibberellic acid, kinetin, indoleacetic acid, and thiourea as potential rest-breaking agents.

5 DNOC is a non-systemic stomach poison and contact insecticide, ovicidal to the eggs of certain insects. It is strongly phytotoxic and its permissible use as an insecticide is limited to dormant sprays or on waste ground. Further, DNOC is known to act as a cumulative poison in man. Although DNOC is relatively inexpensive and effective as a rest-breaking agent, it is toxic enough to limit its continued use and it is currently on the European  
10 Red List of agricultural chemicals which will be prohibited in the future. DNOC is also banned in the United States for use as an agricultural chemical.

One of the most effective alternatives to DNOC is hydrogen cyanamide  
15 according to the publications, Snir, I., "Chemical Dormancy Breaking of Red Raspberry," HortScience, 18, pp. 719-713 (1983); North, M.S., "Effects of Cyanamide and DNOC/oil on Budbreak, Yield and Fruit Size of Golden Delicious Apples," S. Afr. J. Plant Soil, 6(3), pp. 176-178 (1989); Stadler, J.D., North, M.S., and Lutze, G.F.A., "Artificial Rest-Breaking of Apricot and  
20 Plum Cultivars Using Hydrogen Cyanamide," J. S. Afr. Soc. Hort. Sci., 1(1), pp. 9-11 (1991); Nee, C.C. and Fuchigami, L.H., "Overcoming Rest at Different Growth with Hydrogen Cyanamide," Scientia Horticulturae, 50, pp. 107-113 (1992); and North, M.S., "Alternative Rest-Breaking Agents to DNOC/oil for Apples," S. Afr. J. Plant Soil, 9(1), pp. 39-40 (1992).

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Hydrogen cyanamide is a skin and eye irritant and is especially acute when used in combination with the consumption of alcohol. The toxicity and

relatively high price limit its market acceptance and hydrogen cyanamide has also been placed on the European Red List.

Thus, there exists an immediate need for new, milder rest-breaking agents, not only in South Africa, but also in countries which are currently developing agricultural industries but do not have an ideal climate therefor, such as Brazil. Further, there is a need for such new rest-breaking agents in countries with existing agricultural industries that, up to now, did not appreciate the extent of the problem of delayed foliation.

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The response of a plant to a rest-breaking agent is dependent upon the chemical composition of the agent, its application rate and timing and on the nutritional status of the plant according to Terblanche, J.H. and Strydom, D.K., "Effects of Autumnal Nitrogen Nutrition, Urea Sprays and a Winter Rest-Breaking Spray on Budbreak and Blossoming of Young "Golden Delicious" Trees Grown in Sand Culture," Deciduous Fruit Grower, 23, pp. 8-14 (1973).

Many chemicals have been found to have rest-breaking ability. A summary of some of these chemicals can be found in Saure, M.C., "Dormancy Release in Deciduous Fruit Trees," Janick, J. (Ed.), Horticultural Reviews, 7, pp. 239-287, AVI Publishing Co. Inc., Westport, Connecticut (1985). The efficacy of these various rest-breaking agents appears to be directly related to their physiological harshness.

25

One of the milder rest-breaking agents is potassium nitrate which has been shown to have a positive effect on peaches. Generally, fruit trees having a lower chill requirement, such as peaches, also require lower concentrations

of rest-breaking agents, whereas fruits with a higher chill requirement, such as apples, require excessive concentrations of a mild rest-breaking agent. Articles demonstrating the effects of thiourea, potassium nitrate, and combinations thereof include Wolak, R.J. and Couvillon, G.A., "Time of  
5 Thiourea-KNO<sub>3</sub> Application on the Rest Requirement and Bud Development in 'Loring' Peach," HortScience, 11(4), pp. 400-402 (1976) and Fernandez-Escobar, R. and Martin, R., "Chemical Treatments for Breaking Rest in Peach in Relation to Accumulated Chilling," J. Hort. Sci., 62(4), pp. 457-461 (1987).

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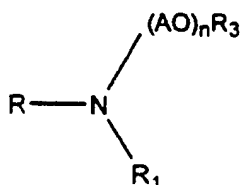
For the foregoing reasons, there exists a need in the art for improved rest-breaking agents which are, affordable, effective, less toxic than the present rest-breaking agents and which can be employed in reasonable concentrations.

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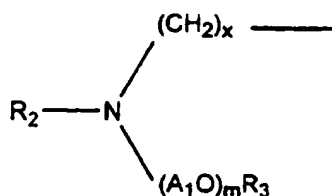
#### Summary of the Invention

The present invention relates to a process for enhancing the rest-breaking in deciduous fruit trees which comprises the step of applying to at least one  
20 deciduous fruit tree, before blossom, an effective amount of at least one rest-breaking agent selected from the group of calcium nitrate, ammonium nitrate, calcium ammonium nitrate, urea ammonium nitrate, and zinc ammonium nitrate, and a compound selected from the group consisting of alkoxyated amines represented by the following general formula:

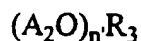
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wherein  $n$  is an integer from 1 to 50,  $A$  represents an alkylene group and when  $n > 1$ , each  $A$  may be the same or different alkylene groups,  $R$  is selected from straight or branched chain alkyl or alkenyl groups having 8 to 22 carbon atoms and groups represented by the formula:



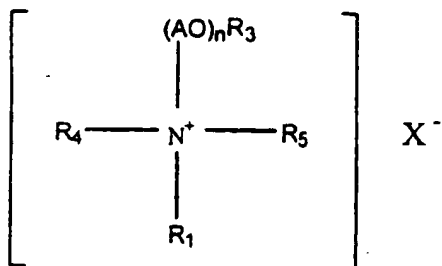
wherein  $m$  is an integer from 1 to 50,  $A_1$  represents an alkylene group and when  $m > 1$ , each  $A_1$  may be the same or different alkylene groups,  $x$  is an integer from 1 to 6, and  $R_2$  is selected from straight or branched chain alkyl or alkenyl groups having 8 to 22 carbon atoms,  $R_3$  is selected from hydrogen, straight or branched chain alkyl and alkenyl groups having 1 to 8 carbon atoms and aryl groups having up to 8 carbon atoms; and  $R_1$  is selected from hydrogen, straight or branched chain alkyl and alkenyl groups having 1 to 22 carbon atoms, and a group represented by the formula:



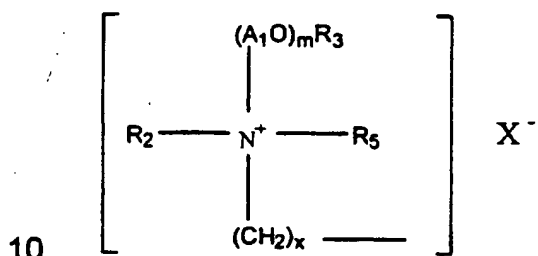
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wherein  $n'$  is an integer from 1 to 50,  $A_2$  represents an alkylene group and when  $n' > 1$ , each  $A_2$  may be the same or different alkylene groups; and  $R_3$  is as defined above, and alkoxylated quaternary ammonium compounds represented by the following general formula:

25



wherein n, A, R<sub>1</sub> and R<sub>3</sub> are as defined above, X is an anion, R<sub>5</sub> is selected from hydrogen, straight or branched chain alkyl or alkenyl groups having 1 to 4 carbon atoms, and benzyl, or R<sub>5</sub>X<sup>-</sup> is carboxy methyl as in betaines or oxygen as in amine oxides; and R<sub>4</sub> is selected from straight or branched chain alkyl and alkenyl groups having 8 to 22 carbon atoms and groups represented by the formula:



wherein A<sub>1</sub>, m, R<sub>2</sub>, R<sub>3</sub>, R<sub>5</sub>, X, and x are as defined above.

More particularly, X may be halides such as Cl<sup>-</sup>, Br<sup>-</sup>, CH<sub>3</sub>SO<sub>4</sub><sup>-</sup>, and C<sub>2</sub>H<sub>5</sub>SO<sub>4</sub><sup>-</sup>, among others. The anion associated with these quaternary ammonium compounds is not critical to the process of the present invention.

The use of the above-identified compounds as adjuvants for chemical rest-breaking agents in deciduous fruit trees is disclosed in WO 94/23574.



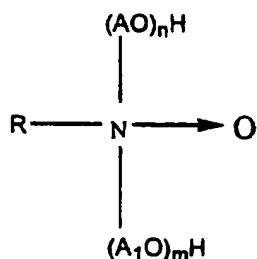
However, the specific combination of the rest-breaking agents and adjuvants according to the present invention and its beneficial properties are neither disclosed nor suggested in said reference.

- 5 The above-identified compounds are further described in EP-A-0 463 241 as useful blossom thinning agents for stone fruits. In addition, a small group of the foregoing compounds are known from European patent 0 257 686 which discloses several alkoxyated amines and their use as activity promoting additives for herbicides and fungicides. Also disclosed
- 10 therein is a method for making these compounds, which method is hereby incorporated by reference.

Preferably, R is selected from alkyl groups having 12-22 carbon atoms

- 15 Preferably, the molecular weight of the compounds used in the present invention is less than 8000 grams/mole though higher molecular weight compounds can be employed in some circumstances.

- In the process of the present invention, quaternary ammonium compounds
- 20 include also amine oxides as in the following general formula:



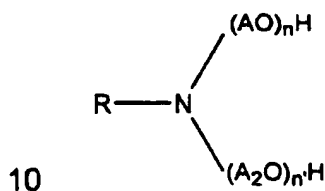
wherein R, A, A<sub>1</sub>, n and m are as defined above.

Typical compounds suitable for use in the process of the present invention include, but are not limited to, coco bis(2-hydroxyethyl) methyl ammonium chloride, polyoxyethylene (15) coco methyl ammonium chloride, oleyl bis(2-hydroxyethyl) methyl ammonium chloride, polyoxyethylene (15) stearyl methyl ammonium chloride, coco bis(2-hydroxyethyl) amine, polyoxyethylene (5) coco amine, polyoxyethylene (15) coco amine, tallow bis(2-hydroxyethyl) amine, polyoxyethylene (5) tallow amine, polyoxyethylene (15) tallow amine, tallow/oleyl bis(2-hydroxyethyl) amine, oleyl bis(2-hydroxyethyl) amine, polyoxyethylene (5) oleyl amine, polyoxyethylene (15) oleyl amine, hydrogenated tallow bis(2-hydroxyethyl) amine, hydrogenated tallow polyoxyethylene (5) amine, hydrogenated tallow polyoxyethylene (15) amine, hydrogenated tallow polyoxyethylene (50) amine, N,N',N'-tris(2-hydroxyethyl)-N-tallow-1,3-diaminopropane, N,N',N'-polyoxyethylene (10) -N-tallow-1,3-diaminopropane, and N,N',N'-polyoxyethylene (15) -N-tallow-1,3-diaminopropane.

The preferred alkylene oxides for use in the present invention are ethylene oxide, propylene oxide, isobutylene oxide and butylene oxide. The adjuvants of the present invention are made in such a way as to introduce varying numbers of alkylene oxide units onto the amino nitrogen. Thus, these alkylene oxide groups may be all the same, such as, for example, one or more ethylene oxide units, or the groups may be different to form, for example, block copolymer chains of ethylene oxide and propylene oxide units, random copolymer chains consisting of several units of each of two or more different alkylene oxides, or alternating units of two or more alkylene oxides. Any conceivable combination of alkylene oxide units up to 50 units long may be employed at each location on the amino nitrogen

which is to contain such units. In addition, a single amino nitrogen may contain two different alkylene oxide chains attached thereto or two chains which are the same. In a preferred embodiment of the present invention, block copolymer chains of ethylene oxide and one or more of propylene oxide or butylene oxide are employed.

In a more preferred embodiment of the present invention, the compound is an alkoxyated amine represented by the following general formula:



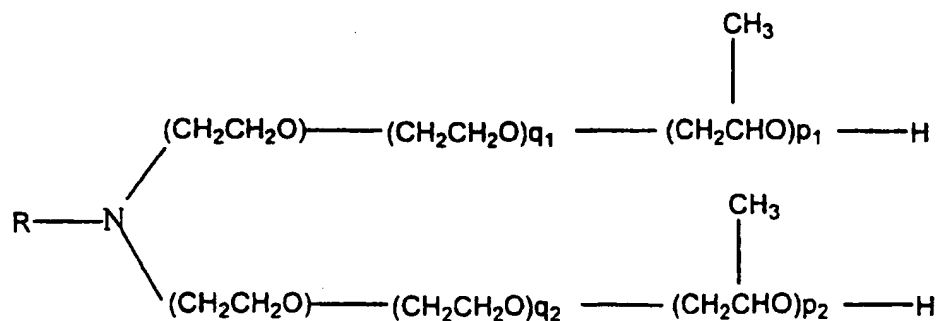
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wherein  $n$  and  $n'$  are integers from 1 to 50,  $A$  and  $A_2$  represent alkylene groups and when  $n$  and/or  $n'$  are greater than 1, each  $A$  and  $A_2$  may be the same or different alkylene groups, and  $R$  is selected from straight or branched chain alkyl or alkenyl groups having 8 to 22 carbon atoms.

15

Most preferred is a tallowamine is employed containing five moles of ethylene oxide derived units and a total of 12 moles of propylene oxide units, which can be represented by the general formula:

20



wherein  $(p1+p2)=12$ ,  $(q1+q2)=3$  and R is a hydrocarbon group derived from tallow fatty acid. This compound is also known as Armobreak®.

- 5 The rest-breaking activity of calcium nitrate, ammonium nitrate, calcium ammonium nitrate, urea ammonium nitrate, zinc ammonium nitrate, and combinations thereof, in deciduous fruit trees was not known up to now. These nitrates are milder agents for which the activity can be enhanced to the desired level by the adjuvants defined above. Accordingly, the process
- 10 of the present invention is useful for rest-breaking of deciduous fruit trees to produce improvements in advancing the time of bloom, budbreak and/or leaf cover and fruit set. The present process also enables the use of said rest-breaking agents in smaller quantities.
- 15 Examples of the type of fruit trees to which the present invention is applicable are apples, pears, peaches, apricots, nectarines, plums e.g. Japanese plums, cherries e.g. Japanese cherries, and kiwis.

When reference is made in this patent application to enhancement of rest-

20 breaking, what is meant is that the time of bloom is advanced or one or more budbreak and/or leaf cover or fruit set are improved over a control tree.

The process of the present invention is to be applied to the deciduous fruit

25 trees prior to blossom. The process is particularly useful in growing areas where the winter chilling of the fruit trees is insufficient to provide good budbreak and fruit set for the particular cultivar. Winter chilling can be measured and is often represented by the unit, "Richardson Chill Units."

The optimum time to break rest for a particular deciduous fruit tree will depend upon several factors including the type of fruit, the cultivar, the climatic conditions and the type and amount of rest-breaking agent being applied. For some fruit or cultivar species, the best rest-breaking effects are accomplished by early application of the rest-breaking agent to the trees whereas for others it is best to wait until just before blossom. In general, the rest-breaking agent will be applied at some point between the time when winter has peaked and the time when blossoming begins.

10

One of the effects of the rest-breaking agents of the present invention is to accelerate the blossoming of the fruit trees. Accordingly, in the application of these rest-breaking agents consideration should be given to this effect and the agents should not be applied too early such that blooming occurs when there is still a risk of harsh weather.

15

The process of the present invention is carried out by the application of an effective amount of at least one rest-breaking agent selected from the group of calcium nitrate, ammonium nitrate, calcium ammonium nitrate, urea ammonium nitrate, and zinc ammonium nitrate, in combination with an amount of at least one activity promoting compound as defined herein to enhance the rest-breaking activity of said rest-breaking agent.

20

If desired, a combination of rest-breaking agents may be used in conjunction with one or more adjuvants as defined herein, said combination comprising at least one rest-breaking agent as defined above and one or more known rest-breaking agents. Examples of known rest-breaking

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agents include hydrogen cyanamide, potassium nitrate, the potassium salt of gibberellic acid, kinetin, indoleacetic acid, and thiourea.

5 The rest-breaking agents are preferably applied in the form of an aqueous solution in a concentration of 0.25 to 30 vol.% and more preferably from 0.5 to 10 vol.%. The lower limit is generally determined by the upper limit on application volume for the particular application equipment being employed, as well as by the type of fruit, the cultivar and the particular rest-breaking composition.

10

The upper concentration limit will generally be dictated by phytotoxicity considerations since higher concentrations of certain compounds have a localized phytotoxic effect on the trees. Thus, a concentration should be selected which provides adequate rest-breaking without unwanted  
15 phytotoxic effects on the remainder of the plant. Such concentrations can be selected by routine experimentation with the particular species of plant.

The activity promoting additive of the present invention is generally employed in a concentration of 0.1-10.0 vol.% in the aqueous solution and  
20 more preferably, 0.2-5.0 vol.%. Again, the amount of activity promoting additive required will depend on the fruit, the cultivar and the particular rest-breaking agent, as well as the quantity of rest-breaking agent to be employed.

25 The composition is preferably applied in a manner similar to the manner in which commercial insecticides are applied. More particularly, conventional equipment such as knapsack sprayers, hand held spray guns, mist blowers, and aerial spraying equipment among others may be used. The

Table 1

| Example | Composition                                    | Bud break |
|---------|--|-----------|
|         |  |           |
| A       | 2% W. Oil                                      | 62.9      |
| B       | 6% DNOC/ W. Oil                                | 62.7      |
| C       | 0.5% Dormex + 2% W. Oil                        | 53.9      |
| D       | 1.5% Armobreak + 8 wt% KNO <sub>3</sub>        | 58.4      |
| 1       | 1.5% Armobreak + 3% UAN + 1% ZAN               | 70.1      |
| 2       | 1.5% Armobreak + 2% UAN + 4% CaNO <sub>3</sub> | 72.6      |

W. Oil = winter oil

DNOC = dinitro ortho cresol

5 Dormex = hydrogen cyanamide rest-breaking agent

UAN = urea ammonium nitrate

ZAN = zinc ammonium nitrate

- 10 These results demonstrate that the compositions of the present invention significantly improve the bud break compared with the prior art compositions.

#### Examples 3 and 4 and Comparative Examples E-H

15

The effect of Armobreak® and rest-breaking agents according to the present invention were tested in Topred Apples in South Africa together with compositions of the prior art. The compositions were sprayed 6 weeks before estimated full bloom. Results are listed in Table 2.

composition is applied the same way as in pesticide application. The compositions may also be applied directly to the plant by hand, if desired.

The process of the present invention has the significant advantages that it  
5 breaks rest to the extent that the use of known, highly toxic rest-breaking agents can be eliminated or considerably reduced, it can be done in a manner which is safe for the crops and the treatment has no long term phytotoxic effect on the plants, if carried out correctly. Further, the rest-breaking process will cause significantly less harm to beneficial insects  
10 when applied within the normal application volume, and the process appears to be environmentally acceptable, non-hazardous to operators of the application equipment, and non-corrosive to the equipment.

The present invention will be further illustrated by the examples appended  
15 hereto.

#### Examples 1 and 2 and Comparative Examples A-D

The effect of Armobreak® and rest-breaking agents according to the  
20 present invention were tested on Granny Smith Apples in South Africa and compared with the effect of compositions of the prior art.

All materials were applied 6 weeks before estimated full bloom. Results are listed in Table 1. All amounts are volume percent, based on the total  
25 volume of the aqueous solution, except if indicated otherwise. The results for budbreak represent the absolute amount of budbreak (amount of budding per tree).



Table 2

| Example | Composition                                    | Bud break |
|---------|--|-----------|
|         |  |           |
| E       | 2% W. Oil                                      | 70.99     |
| F       | 6% DNOC/ W. Oil                                | 52.06     |
| G       | 0.5% Dormex + 2% W. Oil                        | 73.05     |
| H       | 1.5% Armobreak + 8 wt% KNO <sub>3</sub>        | 72.49     |
| 3       | 1.5% Armobreak + 3% UAN + 1% ZAN               | 74.77     |
| 4       | 1.5% Armobreak + 2% UAN + 4% CaNO <sub>3</sub> | 77.07     |

W. Oil = winter oil

DNOC = dinitro ortho cresol

5 Dormex = hydrogen cyanamide rest-breaking agent

UAN = urea ammonium nitrate

ZAN = zinc ammonium nitrate

#### 10 Example 5 and Comparative Examples I-L

The effect of Armobreak<sup>®</sup> and rest-breaking agents according to the present invention were tested in Golden Delicious Apples in South Africa together with compositions of the prior art. The compositions were sprayed

15 5 weeks before estimated full bloom. Results are listed in Table 3.

Table 3

| Example | Composition                             | Bud break |
|---------|---|-----------|
|         |   |           |
| I       | 6% DNOC/ W. Oil                         | 79.6      |
| J       | 0.5% Dormex + 2% W. Oil                 | 75.1      |
| K       | 1.5% Armobreak + 8 wt% KNO <sub>3</sub> | 69.9      |
| L       | 2% W. Oil + 8 wt% KNO <sub>3</sub>      | 66.3      |
| 5       | 1.5% Armobreak + 3% UAN + 1% ZAN        | 80.5      |

W. Oil = winter oil

5 DNOC = dinitro ortho cresol

Dormex = hydrogen cyanamide rest-breaking agent

UAN = urea ammonium nitrate

ZAN = zinc ammonium nitrate

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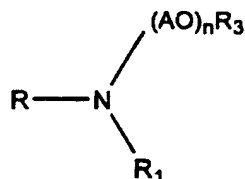
#### Example 6 and Comparative Examples M-N

15 The effect of Armobreak® and rest-breaking agents according to the present invention were tested on Flavortop nectarines in South Africa together with compositions of the prior art. Flavortop is a cultivar with a high chilling requirement, i.e. it needs a relatively cold winter to avoid delayed foliation in spring. The compositions were sprayed 2 weeks before estimated full bloom. Results are listed in Table 4.

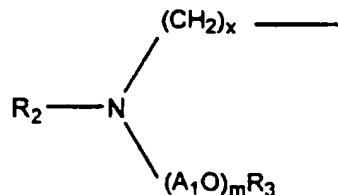
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## CLAIMS

1. A process for breaking the rest in deciduous fruit trees which comprises the step of applying to at least one deciduous fruit tree before blossom, an effective amount of at least one rest-breaking agent selected from the group of calcium nitrate, ammonium nitrate, calcium ammonium nitrate, urea ammonium nitrate, and zinc ammonium nitrate, and a compound selected from the group consisting of alkoxylated amines represented by the following general formula:



- wherein  $n$  is an integer from 1 to 50,  $A$  represents an alkylene group and when  $n > 1$ , each  $A$  may be the same or different alkylene groups,  $R$  is selected from straight or branched chain alkyl or alkenyl groups having 8 to 22 carbon atoms and groups represented by the formula:



- wherein  $m$  is an integer from 1 to 50,  $A_1$  represents an alkylene group and when  $m > 1$ , each  $A_1$  may be the same or different alkylene

5

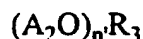
Table 4

| Example | Composition                           | Bud break | g/fruit |
|---------|---------------------------------------|-----------|---------|
|         |                                       |           |         |
| M       | Control                               | 22        | 108     |
| N       | 2% Armobreak + 4 wt% KNO <sub>3</sub> | 26        | 122     |
| 6       | 2% Armobreak + 4% UAN                 | 37        | 124     |

UAN = urea ammonium nitrate

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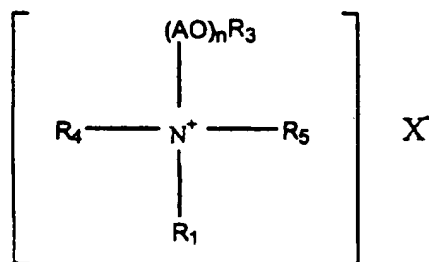
groups,  $x$  is an integer from 1 to 6, and  $R_2$  is selected from straight or branched chain alkyl groups having 8 to 22 carbon atoms,  $R_3$  is selected from hydrogen, straight or branched chain alkyl and alkenyl groups having 1 to 8 carbon atoms and aryl groups having up to 8 carbon atoms; and  $R_1$  is selected from hydrogen, straight or branched chain alkyl and alkenyl groups having 1 to 22 carbon atoms, and a group represented by the formula:



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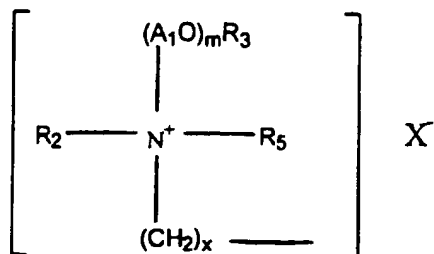
wherein  $n'$  is an integer from 1 to 50,  $A_2$  represents an alkylene group and when  $n' > 1$ , each  $A_2$  may be the same or different alkylene groups, and  $R_3$  is as defined above; and alkoxylated quaternary ammonium compounds represented by the following general formula:

15



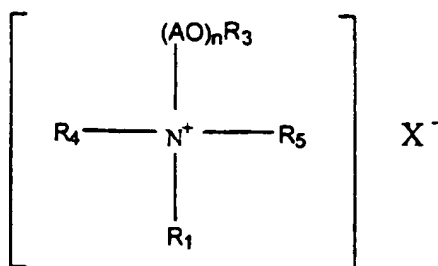
20

wherein  $n$ ,  $A$ ,  $R_1$  and  $R_3$  are as defined above,  $X$  is an anion,  $R_5$  is selected from hydrogen, straight or branched chain alkyl or alkenyl groups having 1 to 4 carbon atoms, and benzyl, or  $R_5X^-$  is carboxy methyl or oxygen; and  $R_4$  is selected from straight or branched chain alkyl and alkenyl groups having 8 to 22 carbon atoms and groups represented by the formula:



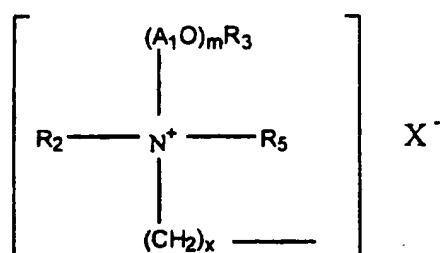
wherein A1, m, R<sub>2</sub>, R<sub>3</sub>, R<sub>5</sub>, X, and x are as defined above.

- 5    2.    The process of claim 1 wherein a rest-breaking composition is applied in the form of an aqueous solution having a concentration of from 0.1 to 10 vol.% of said compound and from 0.25-30 vol.% of said rest-breaking agent.
- 10   3.    The process of claim 2 wherein said compound has a molecular weight of less than 8000 grams/mole.
4.    The process of claim 3 wherein said compound is an alkoxyated quaternary ammonium compound represented by the general formula:
- 15

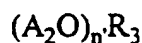


wherein n is an integer from 1 to 50, X is an anion, A represents an alkylene group and when n>1, each A may be the same or different

alkylene groups,  $R_5$  is selected from hydrogen, straight or branched chain alkyl and alkenyl groups having 1 to 4 carbon atoms, and benzyl, or  $R_5X^-$  is carboxymethyl or oxygen; and  $R_4$  is selected from straight or branched chain alkyl or alkenyl groups having 8 to 22 carbon atoms and groups represented by the formula:

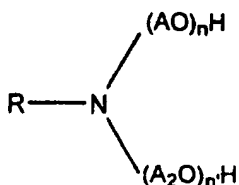


wherein  $m$  is an integer from 1 to 50,  $R_5$  and  $X$  are as defined above,  $A_1$  represents an alkylene group and when  $m > 1$ , each  $A_1$  may be the same or different alkylene groups,  $x$  is an integer from 1 to 6, and  $R_2$  is selected from straight or branched chain alkyl or alkenyl groups having 8 to 22 carbon atoms;  $R_1$  is selected from hydrogen, straight or branched chain alkyl or alkenyl groups having 1 to 22 carbon atoms, and a group represented by the formula:



wherein  $n'$  is an integer from 1 to 50 and  $A_2$  represents an alkylene group and when  $n' > 1$ , each  $A_2$  may be the same or different alkylene groups, and  $R_3$  is selected from hydrogen, straight or branched chain alkyl or alkenyl groups having 1 to 8 carbon atoms and aryl groups having up to 8 carbon atoms.

5. The process of claim 3 wherein said compound is an alkoxyated amine represented by the following general formula:

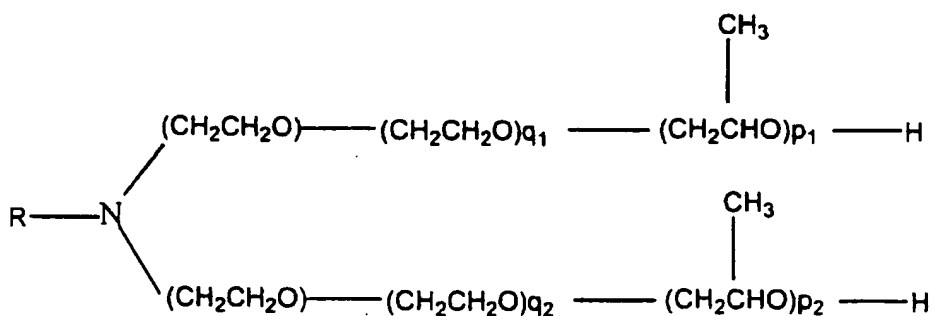


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wherein n and n' are integers from 1 to 50, A and A<sub>2</sub> represent alkylene groups and when n and/or n' are greater than 1, each A and A<sub>2</sub> may be the same or different alkylene groups, and R is selected from straight or branched chain alkyl or alkenyl groups having 8 to 22 carbon atoms.

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6. The process of claim 5 wherein the alkoxyated amine is represented by:

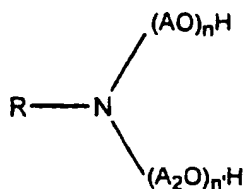


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wherein (p<sub>1</sub>+p<sub>2</sub>)=12, (q<sub>1</sub>+q<sub>2</sub>)=3 and R is a hydrocarbon group derived from tallow fatty acid.

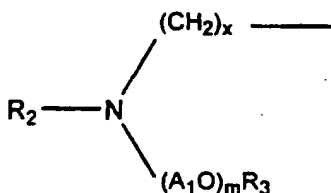
- 20 7. The process of claim 3 wherein said compound is an alkoxyated amine represented by the following general formula:





5

wherein  $n$  and  $n'$  are integers from 1 to 50,  $A$  and  $A_2$  represent alkylene groups and when  $n$  and/or  $n'$  are greater than 1, each  $A$  and  $A_2$  may be the same or different alkylene groups, and  $R$  is a group represented by the formula:

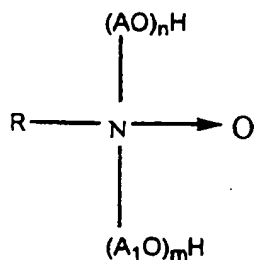


10

wherein  $m$  is an integer from 1 to 50,  $A_1$  represents an alkylene group and when  $m > 1$ , each  $A_1$  may be the same or different alkylene groups;  $x$  is an integer from 1 to 6, and  $R_2$  is selected from straight or branched chain alkyl or alkenyl groups having 8-22 carbon atoms.

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8. The process of claim 3 wherein  $R$  is selected from alkyl groups having 12-22 carbon atoms.
- 20 9. The process of claim 3 wherein said compound is an amine oxide represented by the following general formula:



wherein R, A, A<sub>1</sub>, n and m are as defined in claim 1.

- 5    10.    A composition useful for breaking the rest in deciduous fruit trees  
which comprises an effective amount of at least one rest-breaking  
agent selected from the group of calcium nitrate, ammonium nitrate,  
calcium ammonium nitrate, urea ammonium nitrate, and zinc  
10    ammonium nitrate and at least one compound selected from the  
group of alkoxylated amines, quaternary ammonium compounds and  
amine oxides as defined in any one of claims 1 to 9.

## INTERNATIONAL SEARCH REPORT

National Application No.

PCT/EP 96/05880

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A01N33/08 A01N33/12 A01N33/24 A01N59/00 A01N59/06  
A01N59/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|------------|---|-----------------------|
| X,P        | WO,A,96 01049 (AKZO NOBEL) 18 January 1996<br>see page 15; table 3<br>---   | 10                    |
| Y          | WO,A,94 23574 (AKZO NOBEL) 27 October 1994<br>cited in the application<br>see claims<br>see page 10, line 22 - line 28<br>--- | 1-10                  |
| Y          | US,A,4 001 002 (R.C. BARBA) 4 January 1977<br>see claims 1-3<br>see column 2, line 39 - line 46<br>-----                      | 1-10                  |



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

14 April 1997

Date of mailing of the international search report

22 -04- 1997

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PLI/EP 96/05880

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
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| WO 9601049 A                              | 18-01-96            | AU 2926695 A               | 25-01-96            |
|   |                     | ZA 9505543 A               | 16-02-96            |
| WO 9423574 A                              | 27-10-94            | AU 6569294 A               | 08-11-94            |
|   |                     | BR 9406432 A               | 09-01-96            |
|   |                     | EP 0701399 A               | 20-03-96            |
|   |                     | ZA 9303611 A               | 20-12-93            |
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